

Modulations to molecular high order harmonic generation by electron de Broglie wave

J. Chen^{1*}, Y. J. Chen^{1,3}, J. Fan^{2*}, J. Liu¹, S. G. Chen¹, and X. T. He¹¹ *Institute of Applied Physics and Computational Mathematics,
P.O. Box 8009 (28), Beijing 100088, P. R. China*² *Optical Technology Division,
National Institute of Standards and Technology 100 Bureau Dr.,
Gaithersburg, MD 20899, USA*³ *Graduate School, China Academy of Engineering Physics,
P.O. Box 8009-30, Beijing 100088, P. R. China*

(Dated: February 3, 2008)

We present a new theory that the molecular high order harmonic generation in an intense laser field is determined by molecular internal symmetry and momentum distribution of the tunneling-ionized electron. The molecular internal symmetry determines the quantum interference form of the returning electron inside the molecule. The electron momentum distribution determines the relative interference strength of each individual electron de Broglie wave. All individual electron de Broglie wave interferences add together to collectively modulate the molecular high harmonic generation. We specifically discuss the suppression of the generation on adjacent harmonic orders and the dependence of molecular high harmonic generation on laser intensities and molecular axis alignment. Our theoretical results are in good consistency with the experimental observations.

PACS numbers: 42.65.Ky, 32.80.Rm

Laser-molecule interaction has become an active research area in high field physics. The molecular multi-center structure strongly affects its interaction with the external laser field, resulting in abundant new physics[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Recent studies show that the molecular orbital symmetry strongly affects the single ionization[1, 2, 3]; the nuclei motion in molecular dissociation and Coulomb explosion can be monitored by studying the electron rescattering process[4, 5]; the molecular orbital can be imaged by studying the angular distribution of coincident ion pairs in the molecular double ionization[6]; by studying the spectral profile of molecular high order harmonic emission, one is able to reconstruct the tomography of the molecular structure[9, 11, 12, 13]. Of particular interest is the molecular high order harmonic generation (HHG). The molecular multi-center structure provides the possibility to actively modulate the molecular HHG to generate a single attosecond pulse.

The ionization process of a molecule in an intense laser field is described using the well-known simple-man's model[14]. First one molecular electron tunnels through the potential barrier assisted by the laser field, then the electron in the continuum state may return to the molecular ion as the laser field reverses its phase. Different from the rescattering process in the laser-atom interaction, the multiple atomic sites inside the molecular ion provide multiple options for the electron recombination. The path-differences of the returning electron to the multiple atomic sites result in the interference of electron de Broglie wave ($e^{i\mathbf{k}\cdot\mathbf{r}}$) which significantly affects the molecular ionization and HHG. This was first noticed by Lein and his colleagues in studying the interaction of laser with molecules[15]. Lein *et al.* showed that when recaptured into the bonding orbit of a molecule, the electron waves from the two atomic site emitters (with positions \mathbf{r}_1 and \mathbf{r}_2) interfere as,

$$e^{i\mathbf{k}\cdot\mathbf{r}_1} + e^{i\mathbf{k}\cdot\mathbf{r}_2}, \quad (1)$$

which results in constructive or destructive interference when $\mathbf{k}\cdot\mathbf{R}$ ($\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_2$) is a multiple or a multiple and a half of the laser wavelength. As a result, the n^{th} -order molecular harmonic emission ($n\omega = E_k$, $E_k = k^2/2$) is enhanced (or suppressed).

Recently two experiments were carried out independently to study the HHG of CO_2 in an intense laser field with similar experimental configurations only differing in laser intensities. The suppression of HHG was observed for a range of adjacent harmonic orders in both experiments[16, 17]; while the suppressed harmonic spectral ranges were displaced by about 8 harmonic orders with respect to each other. This cannot be explained by Eq. (1).

In this letter, we present a new theory based on the modified molecular Lewenstein model to describe the laser-molecular interaction. We show that similar to the Young's two-slit interference, the returning electron (tunneling-ionized in the external laser field) wave interferes on the multiple atomic sites inside the molecule ion. The returning

* chen_jing@iapcm.ac.cn; jingyun.fan@nist.gov

electron generally has a momentum (\mathbf{k}) distribution. Each single electron momentum state (the electron de Broglie wave) self-interferes on the multiple atomic sites. All interferences of different electron momentum states (\mathbf{k}) add together to affect the molecular ionization and HHG. The interference structure is uniquely determined by the molecular structure. The electron momentum distribution is a function of laser intensity and molecular axis alignment angle in the external laser field. Thus the molecular HHG changes as laser intensity or molecular axis alignment varies. We also show that molecular HHG at adjacent harmonic orders has similar dependence on electron momentum distribution, thus the suppression or enhancement on molecular HHG occurs over a broad range of adjacent harmonic orders. Our theoretical results agree well with experimental observations.

To directly compare with experimental observations, we study the HHG of CO_2 which has anti-bonding orbital as the highest-occupied state and can be approximately considered as a two-center system when it interacts with the external laser field[16, 17]. Using the molecular Lewenstein model, the dipole acceleration of CO_2 to yield the HHG radiation in an external laser field (polarized along \mathbf{x}) is written as[18, 19, 20, 21],

$$a_x(t) = i \int d^3\mathbf{k} |\Phi_i(\mathbf{k})|^2 \int_0^t dt' A(t') \times E(t) (2 \exp[-iS_0(\mathbf{k}, t, t')] - \exp[-iS_1(\mathbf{k}, t, t')] - \exp[-iS_2(\mathbf{k}, t, t')]) + c.c., \quad (2)$$

where $A(t)$ and $E(t)$ are vector potential and electric field of the laser pulse. Beside the action $S_0(\mathbf{k}, t, t') = \int_{t'}^t dt'' (\frac{1}{2}\mathbf{k}^2 - \mathbf{k} \cdot \mathbf{A}(t'') + I_p)$, two additional action terms $S_1(\mathbf{k}, t, t') = S_0(\mathbf{k}, t, t') - \mathbf{k} \cdot \mathbf{R}$ and $S_2(\mathbf{k}, t, t') = S_0(\mathbf{k}, t, t') + \mathbf{k} \cdot \mathbf{R}$ are introduced accounting for the effects induced by the two O-atomic sites. The three phase terms carrying these actions interfere with each other and modulate the molecular HHG[19, 20, 21, 22]. $\Phi_i(\mathbf{k})$ is the Fourier transformation of the atomic wavefunction φ_i under *linear combination of atomic orbitals-molecular orbitals* (LCAO-MO) approximation in which the molecular wavefunction is expressed as $\psi_i = \varphi_i(\mathbf{r}, -\mathbf{R}/2) - \varphi_i(\mathbf{r}, \mathbf{R}/2)$.

After adopting pole approximation[20] and performing time-integral in Eq. (2), the Fourier transformation of Eq. (2) gives the HHG spectral amplitude of CO_2 [21, 22]

$$S(n) \propto \sum_{l,m} |(e^{i\mathbf{k}' \cdot \frac{\mathbf{R}}{2}} - e^{-i\mathbf{k}' \cdot \frac{\mathbf{R}}{2}}) \Phi_i(\mathbf{k}')|^2 J_l(\frac{-\mathbf{k} \cdot \mathbf{A}_0}{\omega}) J_m(\frac{\mathbf{k} \cdot \mathbf{A}_0}{\omega}), \quad (3)$$

where $J_l()$ is the l^{th} order Bessel function, m and l are numbers of photons that the electron absorbs or emits at ionization or recombination, with $n = m \pm 1 + l$. The electron's momentum is now given as $k^2/2 = (m \pm 1)\omega - I_p$, where I_p is the ionization potential of the molecule. Considering the acceleration effect by bound potential when the electron is in the vicinity of the core, the modified electron momentum k' (parallel to k) is given as $k'^2/2 = k^2/2 + I_p$ [22].

Eq. (3) shows that the molecular HHG is completely determined by the structural factor $(e^{i\mathbf{k}' \cdot \frac{\mathbf{R}}{2}} - e^{-i\mathbf{k}' \cdot \frac{\mathbf{R}}{2}})$ which corresponds to the molecular internal symmetry (here it describes the anti-bonding orbital of CO_2) and the momentum distribution [the rest part of Eq. (3)] of the rescattering electron which is a function of the laser intensity and molecular axis alignment angle (with respect to the direction of the external laser field). Eq. (3) also shows that the electron momentum distribution and consequently the molecular HHG spectral profile vary for different laser intensity and molecular alignment angle. In the following, we numerically study the HHG of CO_2 under various experimental conditions and compare the results with available experimental data.

We first study the contribution to molecular HHG from electron momentum states with momentum \mathbf{k} parallel to \mathbf{E} , because they were considered to contribute the most to the HHG. As shown in Fig. 1, for both harmonic orders $S(n = 13)$ [Fig. 1(a)] and $S(n = 23)$ [Fig. 1(b)], contributions from individual electron momentum states (with \mathbf{k} parallel to \mathbf{E}) are significantly suppressed for smaller k but remain unchanged for big k , when considering the interference effect that is due to the anti-bonding symmetry of CO_2 . An integral of $\int d\Omega \int_0^k k^2 dk$ was then conducted to consider contributions from all electron momentum states. Both $S(n = 13)$ [Fig. 1(c)] and $S(n = 23)$ [Fig. 1(d)] are constant for big k , indicating that the contribution from big- k electron momentum states is negligible. When considering the interference effect, $S(n = 13)$ is relatively suppressed while $S(n = 23)$ is relatively enhanced.

Next we numerically study the variation of HHG spectral profile of CO_2 as a function of laser intensity and molecular alignment angle θ . For fixed laser intensity, the HHG spectral profiles vary for different values of θ as shown in Figs. 2(a) and (b) in which the plots are generated with $I = 1.5 \times 10^{14} \text{ W/cm}^2$ and $I = 2 \times 10^{14} \text{ W/cm}^2$, respectively. Eq. (3) shows that harmonic emissions at adjacent orders have similar dependence on electron momentum contribution. Consequently similar modulations occur on adjacent HHG orders. As shown in Fig. 2(c), with $I = 2 \times 10^{14} \text{ W/cm}^2$ and $\theta = 30^\circ$, HHG is suppressed at a range of adjacent harmonic orders centering at $n = 25$. The center shifts to $n = 35$ for $I = 3 \times 10^{14} \text{ W/cm}^2$ [Fig. 2(d)], qualitatively agreeing with recent experimental observations[16, 17]. (Intensity stabilization and calibration of intense ultrashort laser pulse remain to be a challenge in the experiment.)

To clearly exhibit the dependence of molecular HHG on the laser intensity, we numerically study the HHG at two harmonic orders. For $n = 13$, our numerical results show that the harmonic generation is suppressed at $I = 1.5 \times 10^{14} \text{ W/cm}^2$ [Fig.3(a)] and enhanced at $I = 2 \times 10^{14} \text{ W/cm}^2$ [Fig.3(b)]. For $n = 23$, we show the suppression of harmonic generation at $I = 2 \times 10^{14} \text{ W/cm}^2$ [Fig.3(c)] and enhancement at $I = 3 \times 10^{14} \text{ W/cm}^2$ [Fig.3(d)].

Lastly, it is interesting to find out under what kind of condition the single electron momentum picture given by Lein *et al.* may be used in predicting the suppression position in the HHG spectrum. Examining Eq. (2) shows that if $\mathbf{k} \cdot \mathbf{R}$ (describing the molecular structure) is much smaller than the action S_0 (corresponding to the electron trajectory), then S_0 can be extracted out as a common factor.

The Fourier-transformation of Eq. (2) can now be simplified into Eq. (1). Assuming $\mathbf{A}(t) = \frac{E_0}{\omega} \cos(\omega t)$, we have $S_0 \sim \bar{E}_k T$, where T is the period of the laser field and \bar{E}_k is the average kinetic energy of the electron with $\bar{E}_k \simeq \frac{E_0^2}{2.4\omega^2}$ and $k \simeq E_0/\omega$. Then we reach such a relation

$$R \ll \alpha = E_0/\omega^2, \quad (4)$$

where α is the electron's quiver amplitude in the laser field. Eq. (4) shows that if the electron's quiver amplitude is much larger than the molecular internuclear distance, or in other words, the time difference for the rescattering electron to recombine with the different atomic sites are negligible comparing to the time for electron being in the continuum state, then Eq. (1) can be used to approximately describe the molecular HHG process. Comparing the internuclear distances $R = 2.0 \text{ a.u.}$ for H_2^+ and $R = 4.4 \text{ a.u.}$ for CO_2 with the electron's quiver amplitude of $\alpha = 21 \text{ a.u.}$ in a laser field with intensity of $I = 1.5 \times 10^{14} \text{ W/cm}^2$, it is easy to understand that Eq. (1) gives a better estimation to the suppression of HHG of H_2^+ [15] than to the suppression of HHG of CO_2 .

In conclusion, we develop a new theory about the molecular HHG in an intense laser field. We illustrate that the molecular HHG at each order is contributed by a group of interference effects on the Young's slit (multiple-atomic sites) with each produced by an independent electron de Broglie wave (eigen electron momentum state) and weighed by the electron momentum state amplitude. We show that the single electron momentum picture illustrated by Lein *et al.* is only an approximation of our theory at high laser intensity where the electron's quiver motion amplitude is much larger than the molecular internuclear distance. Our theoretical analysis shows that the difference in the observed suppressed HHG spectral ranges in recent experiments is attributed to the different laser intensities applied in the measurement. We further suggest that the molecular HHG in an intense laser field may be generally described in the form of Eq. (3) by simply replacing the interference factor with the appropriate structure factor of the molecule in use.

This work was supported by the National Natural Science Foundation of China under Grant No. 10574019, 973 research program No. 2006CB806000, ICF research fund under Grant No. 2004AA84ts08, CAEP Foundation No. 2006z0202 and the Multidisciplinary University Research Initiative Center for Photonic Quantum Information Systems (Army Research Office/DTO program DAAD19-03-1-0199).

-
- [1] Talebpour A, Chien C Y and Chin S L 1996 J. Phys. B **29** L677
 - [2] Guo C, Li M, Nibarger J P and Gibson G N 1998 Phys. Rev. A **58** R4271
 - [3] Muth-Böhm J, Becker A and Faisal F H M 2000 Phys. Rev. Lett. **85** 2280
 - [4] Niikura H *et al* 2003 Nature **421** 826
 - [5] Alnaser A S *et al* 2003 Phys. Rev. Lett. **91** 163002
 - [6] Alnaser A S *et al* 2004 Phys. Rev. Lett. **93** 113003
 - [7] Litvinyuk I V *et al* 2003 Phys. Rev. Lett. **90** 233003
 - [8] Zeidler D *et al* 2005 Phys. Rev. Lett. **95** 203003
 - [9] Itatani J *et al* 2004 Nature **432** 867
 - [10] de Nalda R *et al* 2004 Phys. Rev. A **69** 031804(R)
 - [11] Itatani J *et al* 2005 Phys. Rev. Lett. **94** 123902
 - [12] Levesque J *et al* 2007 Phys. Rev. Lett. **98** 183903
 - [13] Le Van-Hoang *et al* 2007 Phys. Rev. A **76** 013414
 - [14] Corkum P B 1993 Phys. Rev. Lett. **71** 1994
 - [15] Lein M *et al* 2002 Phys. Rev. Lett. **88** 183903
Lein M *et al* 2002 Phys. Rev. A **66** 023805
Lein M *et al* 2003 Phys. Rev. A **67** 023819
 - [16] Kanai T, Minemoto S and Sakai H 2005 Nature **435** 470-473
 - [17] Vozzi C *et al* 2005 Phys. Rev. Lett. **95** 153902
Vozzi C *et al* 2006 J. Phys. B **39** S457
 - [18] Le Anh-Thu, Tong X M and Lin C D 2006 Phys. Rev. A **73** 041402(R)

- [19] Chirila C C and Lein M 2006 Phys. Rev. A **73** 023410
 [20] Chen J, Chu Shih-I and Liu J 2006 J. Phys. B. **39** 4747-4758
 [21] Chen Y J, Chen J and Liu J 2006 Phys. Rev. A. **74** 063405
 [22] Chen Y J *et al* Model analysis of two-center interference on high harmonic generation, unpublished.

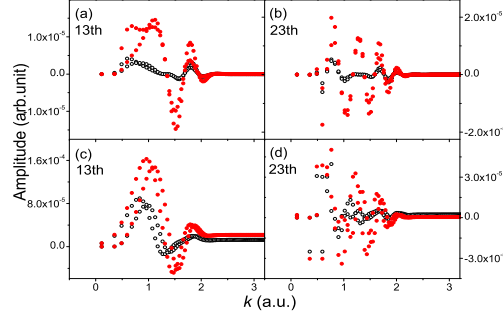


Figure 1: Calculated distributions of contributions to the HHG of CO_2 at $n = 13$ (a) and $n = 23$ (b) from individual electron momentum state with \mathbf{k} parallel to \mathbf{E} , considering (black open dots) and without considering (red filled dots) interference effect. Integrated contributions from various electron momentum states ($\int d\Omega \int_0^k k^2 dk$) to the HHG of CO_2 at $n = 13$ (c) and $n = 23$ (d), considering (black open dots) and without considering (red filled dots) interference effect. $I = 1.5 \times 10^{14} \text{ W/cm}^2$ and $\lambda = 800 \text{ nm}$. (The double-line-structure is due to the double values of k with $k^2/2 = (m \pm 1)\omega - I_p$.)

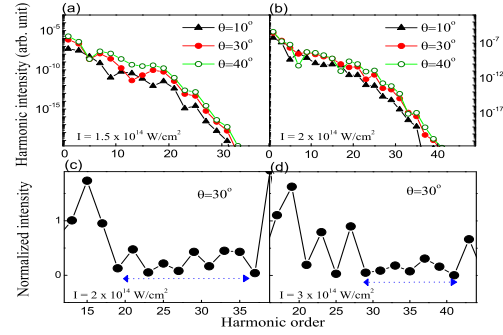


Figure 2: Calculated HHG power spectra of CO_2 at different molecular alignment angles with (a) $I = 1.5 \times 10^{14} \text{ W/cm}^2$ and (b) $I = 2 \times 10^{14} \text{ W/cm}^2$. Calculated HHG suppression (spectra normalized to that averaging over all angles) with (c) $I = 2 \times 10^{14} \text{ W/cm}^2$ and (d) $I = 3 \times 10^{14} \text{ W/cm}^2$. $\lambda = 800 \text{ nm}$.

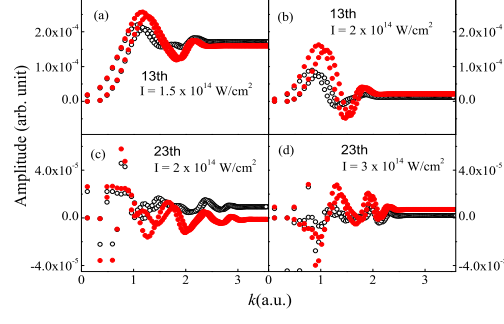


Figure 3: Integrated contributions from various electron momentum states ($\int d\Omega \int_0^k k^2 dk$) to the HHG of CO_2 , considering (black open dots) and without considering (red filled dots) interference effect. (a) $n = 13$ with $I = 1.5 \times 10^{14} \text{ W/cm}^2$ and (b) $n = 13$ and $I = 2 \times 10^{14} \text{ W/cm}^2$, (c) $n = 23$ with $I = 2 \times 10^{14} \text{ W/cm}^2$ and (d) $n = 23$ and $I = 3 \times 10^{14} \text{ W/cm}^2$. $\lambda = 800 \text{ nm}$.